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Soil Manganese Oxide XANES Spectroscopy Pre-edge Feature
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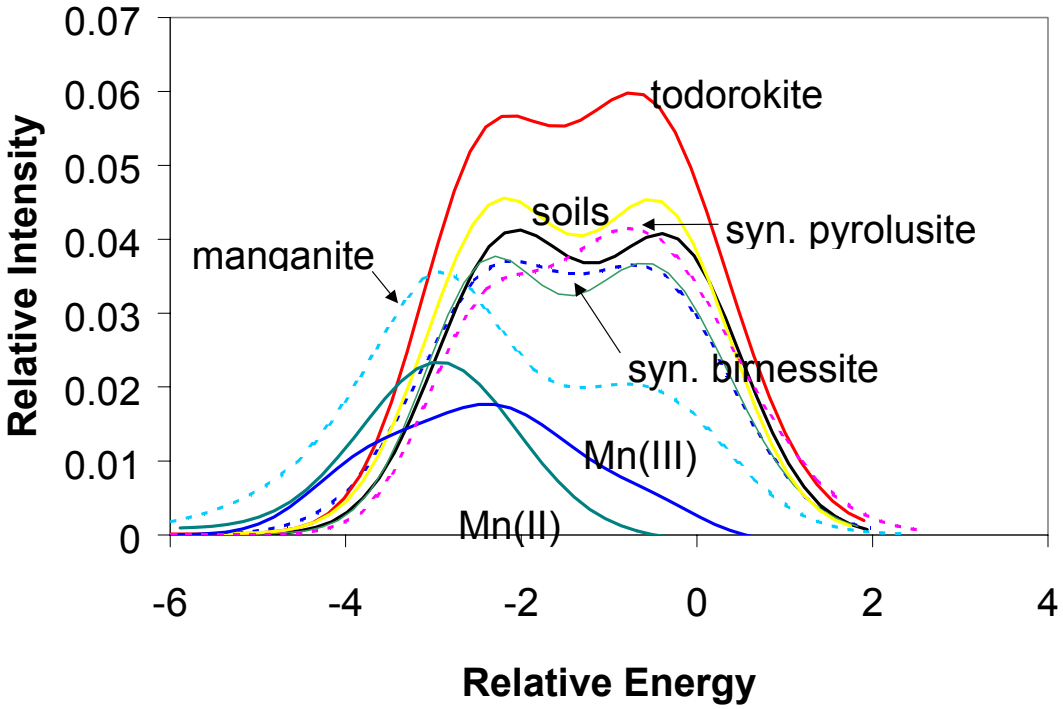
Beamline(s): X26A

Introduction: The structure of soil manganese oxides is difficult to determine because of relatively low concentration and low crystallinity. Mn-XANES spectroscopy is useful for detecting large differences in oxidation states (II vs. III vs. IV) but the shape and position of the main edge is affected by structure. Soil Mn oxides in the aerobic soils we have studied are highly oxidized and have a near edge structure similar to that of synthetic birnessite (Ross et al. 2001). However, other higher oxides also give similar XANES spectra. The pre-edge feature may be a better indicator of oxidation state and may also vary more in intensity among known mineral Mn oxides (Manceau et al. 1992). We have preliminary data from some high-Mn soils and some synthetic standards.
Methods and Materials: Spectra were obtained using the x-ray microprobe at beamline X26A with a spot size of about 20 x 20 um. The energy was calibrated relative to the pre-edge of a Mn(VII) standard. Half-height for the main edge in the higher oxides was 8-9 eV above the Mn(VII) pre-edge. The intensity of Mn fluorescence was normalized to the upper baseline approximately 200-300 eV above the main edge. Spectra were mathematically fit to flatten the baseline.
Results: The pre-edge feature provided separation of oxidation state (see figure) but the energy difference was not as great as found with the main edge. The different synthetic and natural Mn oxides did give different peak intensities and shape (notice the peaks for manganite, which is thought to be a mixture of +II and +IV oxidation states). The soils had spectra of similar shape and intensity to that of synthetic birnessite except that the soil peak were better defined. More work is necessary with additional samples to ensure that the pre-edge feature is consistent. We also need to standardize the baseline adjustment because minor variations have a large effect on peak intensity. If additional runs confirm these initial results, the pre-edge feature could provide a useful tool in differentiating soil Mn oxides.
References:
Manceau A., A.I.Gorshkov, and V.A.Drits. 1992. Structural chemistry of Mn, Fe, Co, and Ni in manganese hydrous oxides: Part I. Information from XANES spectroscopy. Am. Mineral. 77:1133:1144.
Ross D.S., H.C. Hales, G.C. Shea-McCarthy, and A. Lanzirotti. 2001. Sensitivity of soil Mn oxides: XANES spectroscopy may cause reduction. Soil Sci. Soc. Am. J. 65:744-752.



Mn-XANES pre-edge feature of some high-Mn soils and standards.